

学校编码: 10384
学号: 20720100153475

密级

廈門大學

博 士 学 位 论 文

**Co-X (X: V, Ta)基合金热力学数据库的建立
及其合金设计**

**Development of thermodynamic database of Co-X (X: V, Ta)
base alloys and its applications in alloy design**

赵璨璨

指导教师姓名: 王翠萍 教授

专 业 名 称: 材 料 学

论文提交日期: 2015 年 月

论文答辩日期: 2015 年 月

2015 年 月

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果,均在文中以适当方式明确标明,并符合法律规范和《厦门大学研究生学术活动规范(试行)》。

另外,该学位论文为()课题(组)的研究成果,获得()课题(组)经费或实验室的资助,在()实验室完成。(请在以上括号内填写课题或课题组负责人或实验室名称,未有此项声明内容的,可以不作特别声明。)

声明人(签名):

年 月 日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

（ ） 1. 经厦门大学保密委员会审查核定的保密学位论文，于
年 月 日解密，解密后适用上述授权。

（ ） 2. 不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年 月 日

摘要

Co 基合金具有良好的磁学性能、耐磨性、耐热性、耐腐蚀性以及生物相容性，因此在国防和民用工业中是一种重要的金属材料。然而长期以来对新型 Co 基材料的开发通常是凭借经验或是采用试错法，缺乏相应的理论指导，研发周期长，耗资大，效率低。近年来，随着“材料基因组”计划的提出，研究者希望能够重组 Co 基材料的“材料基因”，从而可以根据工业需求来有目的地研发新型 Co 基材料。CALPHAD (CALculation of PHase Diagram)是一种行之有效地获得“材料基因”的方法，基于热力学数据库可以对材料的组织和性能作出预测。目前，专业的钢铁合金、镍基高温合金、铝合金、镁合金、铜合金以及无铅焊接材料热力学数据库均已经被开发并商业化，但还没有一个比较完善的 Co 基合金的热力学数据库。因此，建立关键应用领域 Co 基合金(包括 Co 基高温合金、垂直磁记录材料等)的热力学数据库，无论是对于 Co 基新材料的开发还是对目前已有 Co 基材料的性能改进，都具有重要的理论价值和实际意义。

本研究通过合金法和扩散偶法对部分重要的 Co-X (X: V, Ta)基合金体系的相图进行了实验研究、结合部分已报道的热力学性质及相平衡信息，采用 CALPHAD 方法，对部分重要的 Co 基二元和三元系相图进行了热力学优化与计算，获得了自洽性良好的热力学参数。基于获得的热力学参数，计算的相图与实验相图符合较好。此外，本研究以 Co-V 基磁性薄膜的设计及制备为例，介绍了数据库在材料设计上的应用，研究结果表明该数据库可以为 Co 基材料的研发提供重要的理论指导。以下为本研究的主要内容：

(1) 通过合金法或扩散偶法，采用 EPMA 背散射电子图像组织观察、WDX 成分分析以及 XRD 相结构分析等方法，对 Co-V 二元系、Co-V-Cr (800℃、1000℃、1100℃、1200℃)、Co-V-Fe (800℃、1000℃、1100℃、1200℃)、Co-V-Ni (800℃、900℃、1000℃、1100℃、1200℃)、Co-Ta-Cr (800℃、900℃、1100℃)、Co-Ta-Ni (1200℃、1300℃)、Co-Ta-Fe (1000℃)以及 Fe-Ni-V (1000℃、1100℃、1200℃) 共计 8 个合金体系进行了相平衡的实验测定，获得了共计 22 个等温截面相图。研究结果表明： σ 相在 Co-V-X (X: Cr, Fe, Ni)各三元系中均形成了连续固溶体(化

合物)相; 在 Co-Ta-Cr 三元系中, 高温相 $(\text{Co, Cr})_2\text{Ta}(\text{HT})$ 相在低温段会被稳定化; 本研究测定的全部等温截面相图中均未发现三元化合物相。

(2) 结合本研究所获得的实验结果和文献报道的实验信息, 采用 CALPHAD 方法, 对 Co-V 二元系相图进行了热力学优化与再计算。为了统一热力学模型, 对 Co-Ta、Fe-Ta 及 Ni-Ta 各二元系相图进行了热力学再计算。在本研究及文献报道的实验信息的基础上, 对 Co-V-X (X: Cr, Fe, Ni)、Co-Ta-X (X:Cr, Fe, Ni)以及 Fe-Ni-V、Co-Fe-Ni 和 Cr-Fe-V 各三元系相图进行了热力学优化与计算, 并建立了 Co-X (X: V, Ta)基合金的热力学数据库。

(3) 基于本研究建立的 Co-X (X: V, Ta)基合金的热力学数据库, 对 Co-V 二元及 Co-V 基三元系的 hcp 两相分离的相界线(亦称溶解度间隙)进行了热力学计算, 并分别计算了铁磁性 hcp 相与顺磁性 hcp 相的相分数随成分及温度的变化曲线。在计算结果的基础上, 设计了 Co-V 二元及 Co-V-Ta 三元合金薄膜的成分, 并利用磁控溅射法制备了一系列 Co-V 基合金薄膜, 对其微观组织和磁学性能进行了研究。研究表明: Co-V 二元系中存在亚稳的 hcp 两相分离; Co-V 基合金薄膜的微观组织及磁学性能与计算结果之间存在较好的对应关系; 相图计算对 Co-V 基磁垂直记录材料的设计起到了重要的指导作用。

关键词: Co 基合金; CALPHAD; 相图; 薄膜

Abstract

The cobalt-based alloys play an important role in the defense and civilian industries because they exhibit excellent magnetic properties, wear resistance, heat resistance, corrosion resistance and biocompatibility. In the past decades, the developments of the Co-based alloys were always based on empirical methods or trial-and-error due to the lack of the theories, resulting in a great waste of time and money. In recent years, with the proposal of “Materials Genome Initiative”, researchers expect to purposefully develop new Co-based alloys by rebuilding the “materials genome” of Co-based alloys. CALPHAD (CALculation of PHase Diagram) is an effective method to find the “materials genome”, by which some properties of materials could be predicted based on the thermodynamic database. To date, the thermodynamic databases of steels and Fe-, Ni-, Al-, Mg-, Si-, Cu-based alloys and lead-free soldering materials are commercial, but a systematic thermodynamic database of the Co-based alloys is unavailable. Thus, the foundation of the thermodynamic database of the Co-based alloys is important for the development of the Co-based materials.

In the present work, phase equilibria of some important Co-X (X: V, Ta) base alloy systems were experimentally investigated by using equilibrated alloys and diffusion couples. Based on the experimental data from this work and literatures, some important Co-based systems were thermodynamically assessed by using CALPHAD method. Good agreements are obtained between the calculated results and experimental data. The application on the material design of the thermodynamic database was presented by the design of the Co-V base magnetic recording thin films. The microstructure and magnetic properties of the prepared thin films were investigated. The obtained thermodynamic database may provide useful information for the development of the Co-based alloys. The main contents of this work are listed as follows:

- (1) The phase equilibria in the Co-V binary system, Co-V-Cr (800°C, 1000°C,

1100°C, 1200°C), Co-V-Fe (800°C, 1000°C, 1100°C, 1200°C), Co-V-Ni (800°C, 900°C, 1000°C, 1100°C, 1200°C), Co-Ta-Cr (800°C, 900°C, 1100°C), Co-Ta-Ni (1200°C, 1300°C), Co-Ta-Fe (1000°C) and Fe-Ni-V (1000°C, 1100°C, 1200°C) ternary systems were experimentally researched by BSE images, WDX and XRD analysis. 22 isothermal sections were obtained. The experimental results show that the σ phase forms continuous solid solution in Co-V-X (X: Cr, Fe, Ni) ternary systems, the high-temperature phase (Co, Cr)₂Ta(HT) becomes stable at low temperature in the Co-Cr-Ta ternary system, no ternary compound was found in present work.

(2) Based on the experimental data of present work and literatures, the Co-V binary diagram was thermodynamically calculated by using CALPHAD method. The Co-Ta, Fe-Ta and Ni-Ta binary diagrams were recalculated to build compatible thermodynamic models. Co-V-X (X: Cr, Fe, Ni), Co-Ta-X (X: Cr, Fe, Ni), Fe-Ni-V, Co-Fe-Ni and Cr-Fe-V alloy systems were thermodynamically calculated. The thermodynamic database of Co-X (X: V, Ta) base alloys was established based on the present work and previous works.

(3) Based on the thermodynamic database of Co-X (X: V, Ta) base alloys established in present work, the phase boundary lines of hcp phase separation (miscibility gaps) in the Co-V binary system and Co-V based ternary systems were calculated, the Co-V thin films with different components were deposited by magnetron sputtering. The microstructures and the magnetic properties of thin films were investigated. The experimental results show that the metastable phase separation in the hcp phase exists in the Co-V system, the microstructures and magnetic properties of the thin films consist with the calculated results very well, the CALPHAD method could be effectively used in the design of Co-V based perpendicular magnetic recording media.

Key words: Co-based alloys; CALPHAD; Phase diagram, thin films

目 录

| | |
|--|-----|
| 摘要..... | I |
| Abstract..... | III |
| 第一章 绪论 | 1 |
| 1.1 Co 基合金的主要性能特点及其应用现状 | 2 |
| 1.1.1 Co 基磁性材料 | 2 |
| 1.1.2 Co 基高温合金 | 5 |
| 1.1.3 Co 基耐磨合金与耐腐蚀合金 | 7 |
| 1.2 CALPHAD 方法与 Co 基合金设计 | 8 |
| 1.2.1 CALPHAD 方法简介 | 8 |
| 1.2.2 相图计算的优点 | 10 |
| 1.2.3 Co 基合金相图热力学数据库的研究现状及其应用 | 11 |
| 1.3 研究目的及主要内容 | 12 |
| 参考文献 | 15 |
| 第二章 实验方法及热力学模型 | 24 |
| 2.1 实验方法 | 24 |
| 2.1.1 相平衡测定实验 | 24 |
| 2.1.2 合金薄膜的制备与表征 | 26 |
| 2.2 相图计算的热力学模型 | 27 |
| 2.2.1 纯组元 | 28 |
| 2.2.2 液相 | 28 |
| 2.2.3 端际固溶体相 | 29 |
| 2.2.4 化学计量比化合物 | 30 |
| 2.2.5 金属间化合物溶体相 | 31 |
| 参考文献 | 34 |
| 第三章 Co-V-X (X: Cr, Fe, Ni) 各三元系相图的实验测定及热力学 | |

| | |
|---|-----|
| 计算..... | 35 |
| 3.1 Co-V 二元系相图的实验测定及热力学计算 | 35 |
| 3.1.1 Co-V 二元系相图的研究现状..... | 35 |
| 3.1.2 Co-V 二元系相图的实验测定..... | 36 |
| 3.1.3 Co-V 二元系相图的热力学计算..... | 40 |
| 3.2 Co-V-Cr 三元系相图的实验测定及热力学优化与计算 | 43 |
| 3.2.1 Co-V-Cr 三元系相图的研究现状..... | 43 |
| 3.2.2 Co-V-Cr 三元系相图的实验测定..... | 44 |
| 3.2.2 Co-V-Cr 三元系相图的热力学计算..... | 53 |
| 3.3 Co-V-Fe 三元系相图的实验测定及热力学优化与计算..... | 71 |
| 3.3.1 Co-V-Fe 三元系相图的研究现状..... | 71 |
| 3.3.2 Co-V-Fe 三元系相图的实验测定..... | 73 |
| 3.3.3 Co-V-Fe 三元系相图的热力学计算..... | 81 |
| 3.4 Co-V-Ni 三元系相图的实验测定及热力学优化与计算 | 97 |
| 3.4.1 Co-V-Ni 三元系相图的研究现状..... | 97 |
| 3.4.2 Co-V-Ni 三元系相图的实验测定..... | 99 |
| 3.4.3 Co-V-Ni 三元系相图的热力学计算..... | 103 |
| 3.5 本章小结 | 116 |
| 参考文献 | 118 |
| 第四章 Co-Ta-X (X: Cr, Fe, Ni) 各三元系相图的实验测定及热力学 | |
| 计算..... | 123 |
| 4.1 Co-Ta-Cr 三元系相图的实验测定及热力学计算..... | 123 |
| 4.1.1 Co-Ta-Cr 三元系相图的研究现状 | 123 |
| 4.1.2 Co-Ta-Cr 三元系相图的实验测定 | 125 |
| 4.1.3 Co-Ta-Cr 三元系相图的热力学优化与计算 | 138 |
| 4.2 Co-Ta-Fe 三元系相图的实验测定及热力学计算 | 156 |
| 4.2.1 Co-Ta-Fe 三元系相图的研究现状 | 156 |
| 4.2.2 Co-Ta-Fe 三元系相图的实验测定 | 157 |

| | |
|--|------------|
| 4.2.3 Co-Ta-Fe 三元系相图的热力学优化与计算 | 159 |
| 4.3 Co-Ta-Ni 三元系相图的实验测定及热力学计算 | 169 |
| 4.3.1 Co-Ta-Ni 三元系相图的研究现状 | 169 |
| 4.3.2 Co-Ta-Ni 三元系相图的实验测定 | 170 |
| 4.3.3 Co-Ta-Ni 三元系相图的热力学优化与计算 | 177 |
| 4.4 本章小结 | 187 |
| 参考文献 | 188 |
| 第五章 部分交叉合金体系相图的实验测定及热力学计算 | 195 |
| 5.1 Fe-Ni-V 三元系相图的实验测定及热力学计算 | 195 |
| 5.1.1 Fe-Ni-V 三元系相图的研究现状 | 195 |
| 5.1.2 Fe-Ni-V 三元系相图的实验测定 | 196 |
| 5.1.3 Fe-Ni-V 三元系相图的热力学优化与计算 | 201 |
| 5.2 Co-Fe-Ni 三元系相图的热力学计算 | 209 |
| 5.2.1 Co-Fe-Ni 三元系相图的研究现状 | 209 |
| 5.2.2 Co-Fe-Ni 三元系相图的热力学优化与计算 | 209 |
| 5.3 Cr-Fe-V 三元系相图的热力学计算 | 219 |
| 5.3.1 Cr-Fe-V 三元系相图的研究现状 | 219 |
| 5.3.2 Cr-Fe-V 三元系相图的热力学优化与计算 | 220 |
| 5.4 本章小结 | 225 |
| 参考文献 | 226 |
| 第六章 Co-X (X: V, Ta)基合金热力学数据库的建立及其在垂直磁记录薄膜设计上的应用 | 230 |
| 6.1 Co-X (X: V, Ta)基合金热力学数据库的建立 | 230 |
| 6.2 Co-V 基垂直磁记录薄膜的设计 | 231 |
| 6.2.1 垂直磁记录薄膜的设计原则 | 231 |
| 6.2.2 Co-V 二元合金薄膜的成分与组织设计 | 232 |
| 6.2.3 Co-V-X (X: Cr、Fe、Ni、Ta)三元合金薄膜的成分与组织设计 | 236 |
| 6.3 Co-V 二元合金薄膜成分与组织设计的实验验证 | 242 |

| | |
|---|------------|
| 6.3.1 Co-V 二元合金薄膜的制备 | 242 |
| 6.3.2 Co-V 二元合金薄膜的成分及厚度 | 242 |
| 6.3.3 Co-V 二元合金薄膜的微观组织及结构 | 242 |
| 6.3.4 Co-V 二元合金薄膜的磁学性能 | 246 |
| 6.4 Co-V-Ta 三元合金薄膜成分与组织设计的实验验证 | 253 |
| 6.4.1 Co-V-Ta 三元合金薄膜的制备 | 253 |
| 6.4.2 Co-V-Ta 三元合金薄膜的成分及厚度 | 253 |
| 6.4.3 Co-V-Ta 三元合金薄膜的磁学性能 | 253 |
| 6.5 本章小结 | 270 |
| 参考文献 | 272 |
| 第七章 总结 | 275 |
| 论文的特色和创新之处 | 277 |
| 攻读博士期间取得的学术成果 | 278 |
| 致谢 | 280 |

Table of Contents

| | |
|--|------------|
| Abstract in Chinese..... | I |
| Abstract in English | III |
| Chapter 1 Introduction..... | 1 |
| 1.1 The main characteristics and application status of Co-based alloys..... | 2 |
| 1.1.1 Co-based magnetic materials | 2 |
| 1.1.2 Co-based high-temperature alloys | 5 |
| 1.1.3 Co-based wear-resistant alloys and corrosion-resistant alloys | 7 |
| 1.2 CALPHAD method and Co-based alloys design..... | 8 |
| 1.2.1 Introduction of CALPHAD method..... | 8 |
| 1.2.2 Advantages of CALPHAD method..... | 10 |
| 1.2.3 Research status of Co-based alloy thermodynamic database and its application..... | 11 |
| 1.3 Objective and major contents of this work..... | 12 |
| References..... | 15 |
| Chapter 2 Experimental procedures and thermodynamic models | 24 |
| 2.1 Experimental procedures | 24 |
| 2.1.1 Experimental determination of phase equilibria | 24 |
| 2.1.2 Fabrication and property investigation of the alloy films | 26 |
| 2.2 Thermodynamic models used in this work..... | 27 |
| 2.2.1 Pure elements | 28 |
| 2.2.2 Liquid phase..... | 28 |
| 2.2.3 Solution phases | 29 |
| 2.2.4 Stoichiometric phases | 30 |
| 2.2.5 Extended solid solution..... | 31 |
| References..... | 34 |

Chapter 3 Experimental determination and thermodynamic

calculation of Co-V-X (X: Cr, Fe, Ni) systems.....35

3.1 Experimental determination and thermodynamic calculation of the Co-V binary system.....35

3.1.1 Research status of Co-V binary diagram35

3.1.2 Experimental determination of the Co-V binary system36

3.1.3 Thermodynamic calculation of the Co-V binary system40

3.2 Experimental determination and thermodynamic calculation of the Co-V-Cr system43

3.2.1 Research status of Co-V-Cr ternary system43

3.2.2 Experimental determination of the Co-V-Cr ternary system44

3.2.2 Thermodynamic calculation of the Co-V-Cr ternary system53

3.3 Experimental determination and thermodynamic calculation of the Co-V-Fe system.....71

3.3.1 Research status of Co-V-Fe ternary system71

3.3.2 Experimental determination of the Co-V-Fe ternary system73

3.3.3 Thermodynamic calculation of the Co-V-Fe ternary system81

3.4 Experimental determination and thermodynamic calculation of the Co-V-Ni system.....97

3.4.1 Research status of Co-V-Ni ternary system97

3.4.2 Experimental determination of the Co-V-Ni ternary system99

3.4.3 Thermodynamic calculation of the Co-V-Ni ternary system103

3.5 Conclusions.....116

References.....118

Chapter 4 Experimental determination and thermodynamic

calculation of Co-Ta-X (X: Cr, Fe, Ni) systems123

4.1 Experimental determination and thermodynamic calculation of the Co-Ta-Cr system.....123

| | |
|--|------------|
| 4.1.1 Research status of Co-Ta-Cr ternary system..... | 123 |
| 4.1.2 Experimental determination of the Co-Ta-Cr ternary system..... | 125 |
| 4.1.3 Thermodynamic calculation of the Co-Ta-Cr ternary system..... | 138 |
| 4.2 Experimental determination and thermodynamic calculation of the | |
| Co-Ta-Fe system..... | 156 |
| 4.2.1 Research status of Co-Ta-Fe ternary system..... | 156 |
| 4.2.2 Experimental determination of the Co-Ta-Fe ternary system..... | 157 |
| 4.2.3 Thermodynamic calculation of the Co-Ta-Fe ternary system..... | 159 |
| 4.3 Experimental determination and thermodynamic calculation of the | |
| Co-Ta-Ni system | 169 |
| 4.3.1 Research status of Co-Ta-Ni ternary system..... | 169 |
| 4.3.2 Experimental determination of the Co-Ta-Ni ternary system..... | 170 |
| 4.3.3 Thermodynamic calculation of the Co-Ta-Ni ternary system..... | 177 |
| 4.4 Conclusions..... | 187 |
| References..... | 188 |
| Chapter 5 Experimental determination and thermodynamic | |
| calculation of other important systems..... | 195 |
| 5.1 Experimental determination and thermodynamic calculation of the | |
| Fe-Ni-V system | 195 |
| 5.1.1 Research status of Fe-Ni-V ternary system | 195 |
| 5.1.2 Experimental determination of the Fe-Ni-V ternary system..... | 196 |
| 5.1.3 Thermodynamic calculation of the Fe-Ni-V ternary system | 201 |
| 5.2 Experimental determination and thermodynamic calculation of the | |
| Co-Fe-Ni system | 209 |
| 5.2.1 Research status of Co-Fe-Ni ternary system..... | 209 |
| 5.2.2 Thermodynamic calculation of the Co-Fe-Ni ternary system..... | 209 |
| 5.3 5.2 Experimental determination and thermodynamic calculation of the | |
| Cr-Fe-V system..... | 219 |

| | |
|---|------------|
| 5.3.1 Research status of Cr-Fe-V ternary system..... | 219 |
| 5.3.2 Thermodynamic calculation of the Cr-Fe-V ternary system..... | 220 |
| 5.4 Conclusions..... | 225 |
| References..... | 226 |
| Chapter 6 Development of thermodynamic database of Co-X (X: V, Ta)-based alloys and its applications in the design of perpendicular magnetic recording thin films..... | |
| 6.1 Development of thermodynamic database of Co-X (X: V, Ta)-based alloys..... | 230 |
| 6.2 Design of Co-based perpendicular magnetic recording thin films..... | 231 |
| 6.2.1 Principle in design of perpendicular magnetic recording thin films..... | 231 |
| 6.2.2 Design of the composition and microstructural morphology of Co-V alloy thin films | 232 |
| 6.2.3 Design of the composition and microstructural morphology of Co-V-X (X: Cr、Fe、Ni、Ta) alloy thin films..... | 236 |
| 6.3 Experimental verification of composition and microstructural morphology design of Co-V alloy thin films..... | 242 |
| 6.3.1 Fabrication of Co-V alloy thin films..... | 242 |
| 6.3.2 Composition and thickness of prepared Co-V alloy thin films..... | 242 |
| 6.3.3 Microstructural morphology of Co-V alloy thin films | 242 |
| 6.3.4 Magnetic properties of Co-V alloy thin films..... | 246 |
| 6.4 Experimental verification of composition and microstructural morphology design of Co-V-Ta alloy thin films | 253 |
| 6.4.1 Fabrication of Co-V-Ta alloy thin films..... | 253 |
| 6.4.2 Composition and thickness of prepared Co-V-Ta alloy thin films..... | 253 |
| 6.4.3 Magnetic properties of Co-V-Ta alloy thin films..... | 253 |
| 6.5 Conclusions..... | 270 |
| References..... | 272 |

| | |
|--|------------|
| Chapter 7 Summary | 275 |
| Characteristics and innovations of this work..... | 277 |
| Publications | 278 |
| Appendix..... | 280 |

厦门大学博士论文摘要库

Degree papers are in the “[Xiamen University Electronic Theses and Dissertations Database](#)”.

Fulltexts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to etd@xmu.edu.cn for delivery details.